Jurnal
Teknologi

Full Paper

CHARACTERIZATION OF PCL/ZEOLITE ELECTROSPUN MEMBRANE FOR THE REMOVAL OF SILVER IN DRINKING WATER

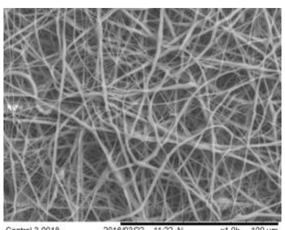
Muhammad Syhamiel Iqhwan Che Rusli[a], Mohd Izzat Hassan[a], Naznin Sultana[a,b*], Ahmad Fauzi Ismail[b]

[a]Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Advanced Membrane Technology Research Center, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

Article history
Received
24 August 2016
Received in revised form
20 October 2016
Accepted
16 December 2016

*Corresponding author
naznin@biomedical.utm.my

Graphical abstract



Abstract

The presence of heavy metals in drinking water leads to several health problems. In this study, polycaprolactone (PCL)/zeolite nano or microfiber electrospun composite membranes, diameter range of the fibers was 2 μm- 6 μm, were fabricated by using electrospinning technique. The membranes separation processes have played very crucial roles in water purification industry. Apart from that, the membranes are prepared with biocompatible, non-toxic materials which will be eco-friendly. In order to produce electrospun membrane, 15% (w/v) of PCL polymer solution was dissolved in acetone and 20% (w/w) zeolite was incorporated into the PCL polymer solution. Electricity charged jet of polymer solution from the syringe formed an electrostatics field when the high voltage of 20kV was applied. Scanning electron micrograph (SEM) and energy dispersive spectroscopy (EDX) implemented to indicate the characterization of membranes. The water contact angle of PCL/zeolite membrane was 119.53±5.24 which was almost same as pure PCL membrane (107.73±8.54). The inducible results obtained in this study suggested that electrospun pcl and polycaprolactone/zeolite layer by layer nanofibrous membranes can be a favored verdict for the removal of heavy metal ions.

Keywords: Polycaprolactone, zeolite, electrospinning, membrane, adsorption

1.0 INTRODUCTION

Water contamination problem has occurred over the years. Economic development and modernization technologies give an impact on the content of water resources [1, 2]. Metals have been exploited into water resources in several ways and aspects. It can be weathering of soil and rocks, volcanic eruptions and from a variety of human activities involving mining, processing and use of metals and/or substances containing metal contaminants. Consequently, human health is affected. Drinking water sources around the globe have contains certain pathogens, organic or inorganic substances that may cause the persistent and chronic effect on consumer's health and ecosystem [3-5]. Researchers have been developing a variety of method to do the investigation and study towards the issues. This is because; water is the basic source of all life on earth [1].

Polycaprolactone (PCL) has known as a nontoxic, accessible, biocompatible and biodegradable synthetic polymer [6] and has been approved for biomedical application by the Food and Drug Administration (FDA) [7] can be manipulated in order to carry out molecular nanofiltration process. It is represented in the formula as ([$C_4H_6O_2$] n) and widely used in biomedical applications. Meanwhile, biodegradable polymers are applicable for long-term sustained delivery of pharmaceutical agents for plenty of applications [8,9]. PCL has various advantages, including mechanical flexibility, low antigenicity, easy processability, and low degrees of chronic persistence. Hydrophobicity and low water absorptivity, toxicity, and low cell attachment and proliferation have been its drawbacks.

Zeolite has been widely explored especially in drug delivery service, petrochemical and plastic industry. Zeolite is microporous, aluminosilicate minerals also commonly used as commercial adsorbents. There are a group of more than 40 crystalline hydrated aluminosilicate minerals. They are based on the structure of three-dimensional network of an aluminum and silicon tetrahedral linked by shared oxygen atoms. Zeolites can be used in various applications as molecular sieves, adsorbents, and catalyst regarding specific pore sizes and large surface areas. Several researchers reported the synthesis of zeolites from a wide variety of starting materials containing high amounts of Si and Al, e.g., kaolin, high-silica bauxite, halloysite, interstratified illitesmectite, montmorillonite, bentonite, and incinerated ash [10].

Silver (Ag) materials can be reincarnated in its metallic or elemental state. However, Ag in the elemental state can go to be oxidized and forms silver cations once exposed to an aqueous environment [15]. Ag containing composites are competently increase wound related problem in higher concentration [16] and increase wound inflammatory response, allergies, skin discoloration [17, 18].

A review article by Balamurugan *et al*. reports on recent trends in nanofibrous membranes and their suitability for air and water filtration applications, preparation and characterization of electrospun nanofibers membranes and their potential applications in water treatment [11]. The polymer and ceramic nanofibers with the different diameter up to nanoscale [19] can be fabricated using electrospinning process which is a versatile technique and applicable for numerous organic and inorganic systems [14]. Another review by Ahn and coworkers [20], they use electrospinning process in order to develop the nanofilters, Nylon 6. In addition, they proved that electrospun membranes are potentially to be explored in application of antimicrobial filters. They have been successfully discovered that electrospun cationomers with quaternary ammonium group against pathogenic bacterial strains of Staphylococcus aureus and Eschericgia coli.

In this paper, we reported the fabrication of layer by layer (PCL and PCL/Zeolite) using multilayer electrospinning method for removal of Silver (Ag) in drinking water. Analytical tools such as scanning electron microscope (SEM), energy dispersive X-ray (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) were used to investigate surface morphology of electrospun membranes and water contact angle (WCA) to examine the membranes' wettability.

2.0 METHODOLOGY

2.1 Materials

Poly (caprolactone) (PCL) (MW: 70,000-90,000) was purchased from Sigma, Beta Zeolite Powder (0.55-0.70 nm pore) (MR: 40) was purchased from ACS Material. Acetone was analytical grade which was used as solvents. Silver nanopowder, <100nm particle size, contains PVP (MW: 107.87) purchased from Sigma.

2.2 Methods

A polymer solution was set up based on the percentage calculation. In order to form 15% w/v of Poly (caprolactone) solution, 1.50g of PCL was dissolved in 10ml of acetone and magnetically stirred at 300 rpm and 50^{0}C for about an hour. On the other hand, 20% w/v or 0.30g of zeolite powder was added into the PCL solution and stirred magnetically at 50°C for another an hour to produce PCL/Zeolite based solution. After that, the mixture solution of PCL and Zeolite was homogenized at the speed of 16~20 1/min x 1000 for about 3 minutes. The membrane was fabricated by electrospinning technique.

Ultrafine nanofibers from micro to nano scale and varied morphologies can be fabricated with ease by a versatile technique called electrospinning [8]. All equipment of the electrospinning has been arranged as shown in Figure 1. After the equipment was ready and safe to conduct, the syringe completed with the tips containing pure 15% PCL polymer solution which should be maintained in liquid form, was placed on a syringe pump. The parameters in Table 1 were followed for the fabrication. A 10cmX10cm of aluminium foil was placed as a collector plate.

For the fabrication of layer by layer (PCL and PCL/Zeolite) membrane, all the steps involved in the electrospinning process were repeated and the parameters remained constant. The duration for the electrospinning process was 1 hour for PCL based solution. After that, the same collector was being used which means that the PCL/Zeolite membrane were collected on top of the PCL membrane. The duration for electrospinning process (PCL/Zeolite) took 1 hour as well, the whole process fabricated the PCL and PCL/Zeolite layer by layer took about 2 hours.

Table 1 Electrospinning parameters

Processing parameters	PCL	PCL/Zeolite
Tip-to-collector distance	10.0cm	10.0cm
Humidity	54.0%	54.0%
Flow rate	3 ml/h	3 ml/h
Voltage Used	20.0 kV	20.0 kV
Duration	1 hour	1 hour
Syringe size	21G	21G

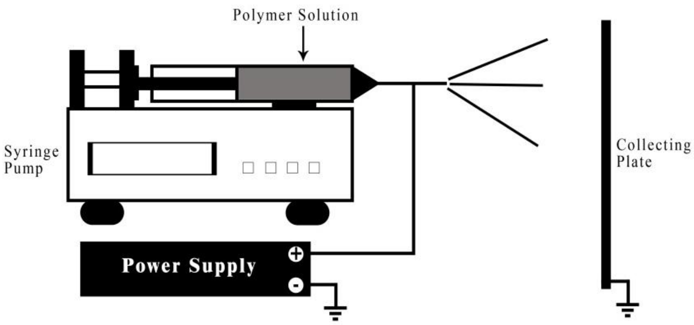


Figure 1 Electrospinning setup

2.3 Characterization

The morphology of PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer by layer membrane constructed were viewed by using a Scanning Electron Microscope (SEM) and also other methods of characterization such as an Energy Dispersive X-ray (EDX), Fourier Transform Spectroscopy (FTIR) and Water Contact Angle (WCA).

2.3.1 Morphology of Membranes

Hitachi-made model TM 3000 was used to observe and characterized the morphology of membrane. These samples were visualized at various magnifications for example 400x, 500x, 1000x, 1500x and 2000x. By regulating the voltage applied, it would extract the clear morphological images. On the other hand, Image J software was utilized to measure the diameter and pores size of fibers. 40 reading of the diameter measurement were taken and the averages were calculated.

2.3.2 Elemental Analysis of Membranes

EDX was used for the elemental analysis or chemical characterization of a sample. EDX enlightened the elements that exist inside the membrane in the form of spectrum. Apart from that, EDX mapping was also carried out to find out the position of specific elements emitting characteristic x-rays. They were interpreted in different colors.

2.3.3 Wettability Analysis

Water contact angle measuring system, VCA Optima, AST Products, Inc. was used to determine the hydrophilicities of PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer by layer membranes. In this process, 3 different measurements for each of the membranes were carried out. The measurements were taken 3 seconds after the droplets of water get contacted with the membrane surface.

2.3.4 Fourier Transform Infra-Red Spectroscopy

Infrared spectrum of absorption or emission of a solid, liquid or gas can be obtained by using Fourier Transform Spectroscopy Infra-Red (FTIR) techniques. FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. A FTIR devices ID5 was used for performing the analysis. The pure zeolite powders were placed on the collector platform. The spectrum of the zeolite powder was analyzed using the OMNIC software. The experiment continued with the next sample, PCL nanofiber membrane and followed by PCL and PCL/Zeolite layer by layer nanofiber membrane. Then, PCL/Zeolite bonding was carried out to complete the analysis on combining these two materials which was the main component of the microfiltration membrane constructed.

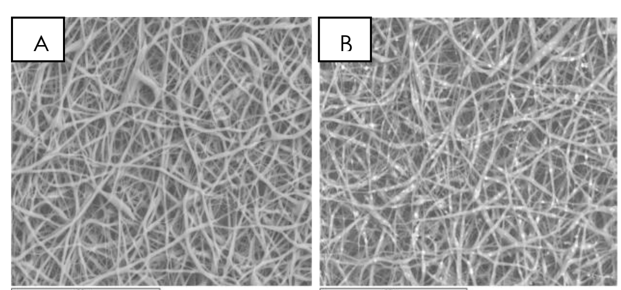
3.0 RESULTS AND DISCUSSION

Table 2 is an observation summary of fiber morphology for PCL, PCL/Zeolite as well as PCL/Zeolite layer by layer. While, Table 4 shows the summary of fiber diameter. Meanwhile, Figure 2 indicates the morphology of fabricated nanofiber membranes.

Table 2 Conditions of fiber diameter observation

Sample	Observation
PCL	No beads
PCL/Zeolite	No beads
PCL/Zeolite layer by layer	No beads

Although the electrospinning process was technically not complex with ease of adaptability, numbers of processing variables need to be controlled in order to generate membrane instead of droplets or beaded morphologies. One of the challenges of the electrospinning process was to optimize the parameters in order to achieve the desirable nanofiber morphology and properties.



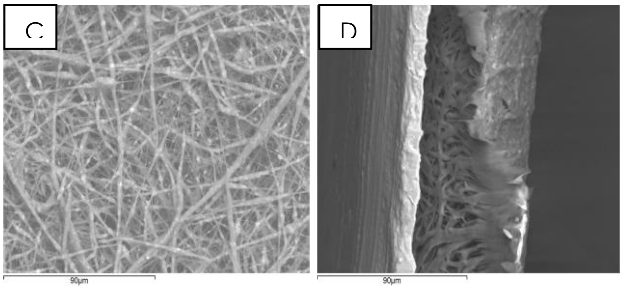


Figure 2 SEM image of (A) 15.0% w/v PCL, (B) 15.0% w/v of PCL and 20.0% w/v of Zeolite membrane, (C) layer by layer PCL and PCL/Zeolite membranes and (D) Cross Section of PCL/Zeolite layer by layer membrane

Electrospun Nanofibers are used for biomedical applications [19], these processing variables can be widely termed as follows: the applied voltage, solution flow-rate, polymer concentration, solution viscosity, nature of solvent, solution conductivity, and the distance between the capillary and collector.
In Table 3 below, the graph frequency of electrospun fiber diameter of the membranes has been analyzed by using Image J software and summarized in chart form order.

From the SEM result, the average diameter range for the pure PCL, PCL/Zeolite as well as PCL/Zeolite layer by layer was in range of 2 µm - 6 µm. The values obtained generally indicated that the membranes were applicable to use as microfiltration unit [20].

Table 3 The distribution of fiber diameters of different membranes

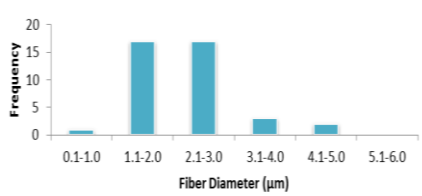
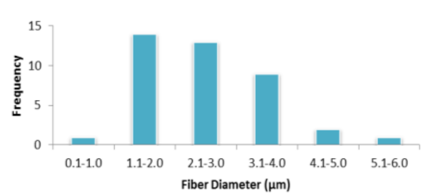
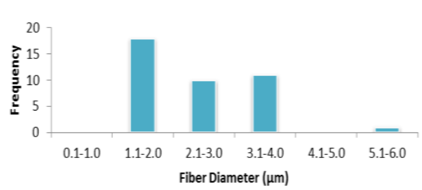
Membranes	Fiber diameter distribution
15.0% w/v PCL	
15.0 % w/v PCL & 20 % w/v Zeolite	
PCL & PCL/Zeolite layer by layer	

Table 4 Average fiber diameters of different membranes

Samples	Average Diameter of Fibers (µm)	Diameter Range of Fibers (µm)
PCL	2.19	0.1 – 5.0
PCL/Zeolite	2.62	0.1 – 6.0
PCL/Zeolite (layer by layer)	2.45	1.1 – 6.0

For the membranes fabricated from pure PCL, existence of carbon and oxygen elements were expected [13]. For that, the resulting spectrum and tabulated results revealed that carbon and oxygen were the predominant components were present in it; with carbon being the most abundant in the selected field. The pure PCL spectrum and element obtained was authenticated and summarized in Table 5 and Figure 3.

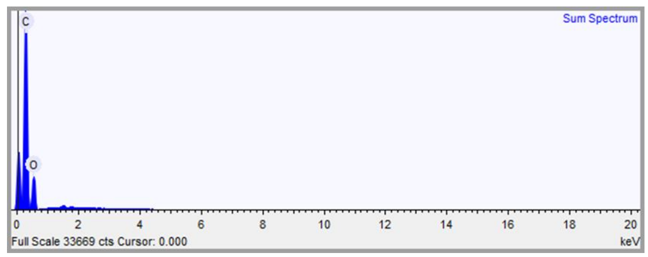


Figure 3 EDX spectrums of PCL electrospun nanofiber

Table 5 Summary results of EDX spectrums of PCL electrospun nanofiber

Element	Weight %	Weight %	Atomic %
Carbon	67.739	0.210	73.662
Oxygen	32.361	0.210	26.338

On the other side, zeolite was defined as an aluminosilicate mineral was expected to have an aluminium or silicon atom inside [10] because “aluminosilicate” term itself referred to the minerals composed of aluminium, silicon, and oxygen, plus countercations. Therefore, Figure 4 and Table 6 showed the summary of elemental analysis conducted for PCL/Zeolite membrane.

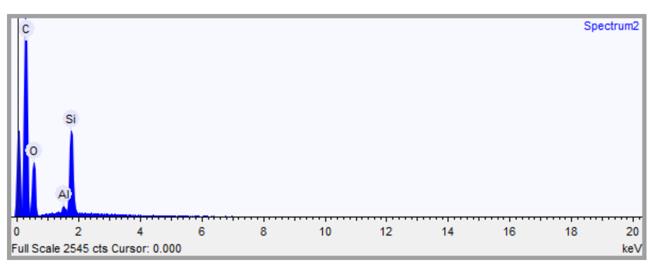


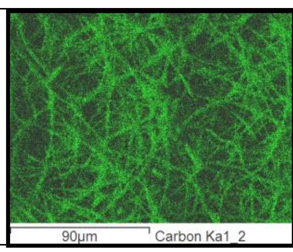
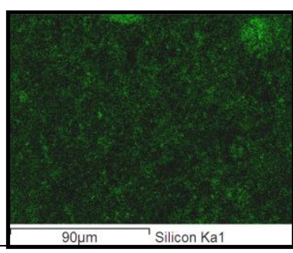
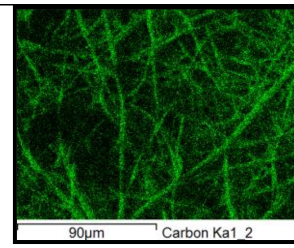
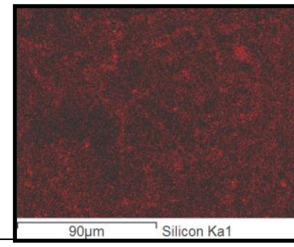
Figure 4 EDX spectrums of PCL/Zeolite electrospun nanofiber

Table 6 Summary results of EDX spectrums of PCL/Zeolite electrospun nanofibers

Element	Weight %	Weight %	Atomic %
Carbon	63.404	0.577	71.518
Oxygen	29.686	0.588	25.139
Aluminum	0.511	0.052	0.256
Silicon	6.399	0.130	3.087

From the EDX employed, the existence of Si and Al atom on the resulting spectra indicated that the membrane of PCL/Zeolite was successfully fabricated. In addition, Si and Al were the aluminosilicate members of the family of microporous solids known as "molecular sieves", suited for microfiltration application. According to IUPAC notation, microporous materials have pore diameters of less than 2 nm or 20 Å (ångströms). Presence of oxygen in zeolite also increased. In term of molecular sieve, zeolites formed purified oxygen from air using its ability to seize impurities, in a process involving the adsorption of nitrogen, leaving highly purified oxygen and up to 5% argon.

Table 7 EDX mapping for PCL, PCL/Zeolite and PCL/Zeolite layer by layer membrane

Membrane	EDX Mapping
PCL	
PCL/Zeolite	
Layer by Layer (PCL and PCL/Zeolite)	 

Another way and useful capability of the EDX technique was x-ray mapping of elements. This technique introduced the position of specific elements emitting characteristic x-rays within an inspection field can be interpreted by unique color. Table 7 is the summary of the EDX element mapping. The color-coded elements aligned with the individual element.

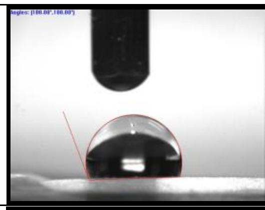
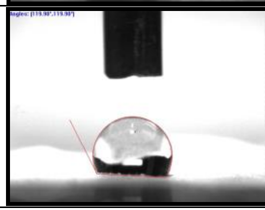
The water contact angle of PCL/zeolite membrane was almost same as pure PCL membrane. The characteristics of pure PCL remains the same as zeolite restored. The lifespan of membrane can be described as same as PCL. The membrane was expected to maintain its mechanical integrity as PCL for several years before completely degraded.

The results in Table 8 of water contact angle for the samples showed that they were having hydrophobic material surfaces. All the tested samples of the electrospun membranes recorded to have more than 90° of contact angle as summarized in Table 9. The higher value of the contact angle indicates the lower wetting tendency.

Table 8 Contact angle of PCL and PCL/Zeolite nanofiber

Samples	Average Contact Angle (°)	Properties
A 15% w/v PCL	107.73±8.54	Hydrophobic
B 15% w/v PCL	119.53±5.24	Hydrophobic

Table 9 Images of contact angle of PCL and PCL/Zeolite

Sample	WCA
A 15% w/v PCL	
B 15% w/v PCL 20% w/v Zeolite	

Meanwhile, Figures 5 describes the FTIR patterns of the PCL, Zeolite and as well as PCL/Zeolite layer by layer membranes. By processing the raw data into the actual spectrum, the bonding occurred at the fabricated membranes can be obtained. The bonding was analyzed by comparing with the data sheet provided of the FTIR patterns. Peak 1070.14 cm^{-1} on zeolite spectrum indicated the T-O-T (T=Al or Si) asymmetric stretching vibration. Meanwhile, at peak 569.8 cm^{-1} show the presence of the double 4 ring (DR4) and peaks were found in 1070.14 cm^{-1} injected an impact on PCL when combining with zeolite [12]. The peak at that value on PCL/Zeolite shortened due to the presences of zeolite, proved the increasing the T-O-T asymmetric stretching vibration of PCL membrane. It is also observed that the presence of the ester group in PCL spectra at peak 1721.09 cm^{-1} which was due to stretching carbonyl [20]. The peaks that exist at peak 2943.82 cm^{-1} and peak 2865.24 cm^{-1} defined the existence of C–H hydroxyl group asymmetric stretching and C-H hydroxyl groups symmetric stretching respectively.

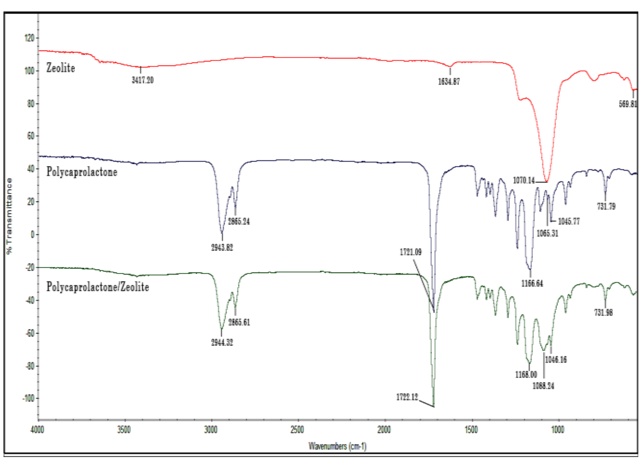


Figure 5 FTIR spectrums of Zeolite, PCL and PCL/Zeolite membrane

4.0 CONCLUSIONS

In this study, the PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer by layer electrospun fibers were successfully fabricated using multilayer electrospinning technique. The purpose of fabricating layer by layer electrospun membrane was to introduce new model of microfiltration unit, biodegerable filter for filtration process. The SEM result showed that homogeneous and beadless membranes were formed for the PCL, PCL/Zeolite as well as PCL and PCL/Zeolite layer layer by layer electrospun fibers.

Acknowledgement

This research is fully supported by HICOE grant vot 4J191. The authors fully acknowledged Ministry of Higher Education (MOHE), RMC, FBME, AMTEC and Universiti Teknologi Malaysia for the approved fund which makes this important research viable and effective.

References

[1] Homaeigohar, S., and Elbahri, M. 2014. Nanocomposite Electrospun Nanofiber Membranes For Environmental Remediation. *Material.* 7(2): 1017-1045.

[2] Nalbandian, M. J., Zhang, M., Sanchez, J., Choa, Y. H., Nam, J., Cwiertny, D. M., & Myung, N. V. 2016. Synthesis And Optimization Of Fe_2O_3 Nanofibers For Chromate Adsorption From Contaminated Water Sources. *Chemosphere.* 144: 975-981.

[3] Ferreira, V., Koricheva, J., Duarte, S., Niyogi, D. K. and Guérold, F. 2016. Effects Of Anthropogenic Heavy Metal Contamination On Litter Decomposition In Streams–A Meta-Analysis. *Environmental Pollution.* 210: 261-270.

[4] Wu, Q., Zhou, H., Tam, N. F., Tian, Y., Tan, Y., Zhou, S., Li, Q., Chen, Y. and Leung, J. Y. 2016. Contamination, Toxicity And Speciation Of Heavy Metals In An Industrialized Urban River: Implications For The Dispersal Of Heavy Metals. *Marine Pollution Bulletin.* 104(1): 153-161.

[5] Li, M., Yang, W., Sun, T. and Jin, Y. 2016. Potential Ecological Risk Of Heavy Metal Contamination In Sediments And Macrobenthos In Coastal Wetlands Induced By Freshwater Releases: A Case Study In The Yellow River Delta, China. *Marine Pollution Bulletin.* 103(1): 227-239.

[6] Jin, R. M., Sultana, N., Baba, S., Hamdan, S. and Ismail, A. F. 2015. Porous PCL/Chitosan and nHA/PCL/Chitosan Scaffolds For Tissue Engineering Applications: Fabrication And Evaluation. *Journal of Nanomaterials*. 1-8.

[7] Lim, M. M., Sun, T. and Sultana, N. 2015 In Vitro Biological Evaluation of Electrospun Polycaprolactone/Gelatine Nanofibrous Scaffold for Tissue Engineering. *Journal of Nanomaterials*. doi:10.1155/2015/303426.

[8] Sultana, N. and Kadir, M. R. A. 2011. Study Of In Vitro Degradation Of Biodegradable Polymer Based Thin Films And Tissue Engineering Scaffolds. *African Journal of Biotechnology*. 10(81):18709-18715.

[9] Sultana, N. and Wang, M. 2007. Fabrication And Characterisation Of Polymer And Composite Scaffolds Based On Polyhydroxybutyrate And Polyhydroxybutyrate-Co-Hydroxyvalerate. *Key Engineering Materials.* 334: 1229-1232.

[10] Mallapur, V. P., Oubagaranadin, J. U. K. and Lature, S. S. 2013. Synthesis Of Zeolite From Inorganic Wastes. *International Journal of Research in Engineering and Technology*. 431-434.

[11] Balamurugan, R., Sundarrajan, S. and Ramakrishna, S. 2011. Recent Trends In Nanofibrous Membranes And Their Suitability For Air And Water Filtrations. *Membranes.* 1(3): 232-248.

[12] Peter, A., Mihaly-Cozmuta, L., Mihaly-Cozmuta, A., Nicula, C., Indrea, E. and Tutu, H. 2012. Calcium-And Ammonium Ion-Modification Of Zeolite Amendments Affects The Metal-Uptake Of Hieracium Piloselloides In A Dose-Dependent Way. *Journal of Environmental Monitoring.* 14(10): 2807-2814.

[13] P. Maiti, A. Rai, S. Senapati, and S. Saraf. 2016. Biodegradable Poly(?-caprolactone) As Controlled Drug Delivery Vehicle Of Vancomycin For The Treatment Of MRSA Infection. *Journal of Materials Chemistry B.* 4(30): 5151-5160.

[14] Ramakrishna, S., Fujihara, K., Teo, W.E., Lim, T. C. and Ma, Z. 2005. *An Introduction To Electrospinning And Nanofibers.* Singapore: World Scientific.

[15] Sterling, J. P. 2014. Silver-Resistance, Allergy, And Blue Skin: Truth Or Urban Legend? *Burns*. 40: S19-S23.

[16] Spacciapoli, P., Buxton, D., Rothstein, D. and Friden, P. 2001. Antimicrobial Activity Of Silver Nitrate Against Periodontal Pathogens. *Journal of Periodontal Research*. 36(2): 108-113.

[17] Boucher, W., Stern, J. M., Kotsinyan, V., Kempuraj, D., Papaliodis, D., Cohen, M. S. and Theoharides, T. C. 2008. Intravesical Nanocrystalline Silver Decreases Experimental Bladder Inflammation. *The Journal of Urology.* 179(4): 1598-1602.

[18] Wasiak, J., Cleland, H., Campbell, F. and Spinks, A. 2013. Dressings For Superficial And Partial Thickness Burns. The Cochrane Library.

[19] Chang, H. C., Sun, T., Sultana, N., Lim, M. M., Khan, T. H., Ismail, A. F. 2016. Conductive PEDOT:PSS Coated Polylactide (PLA) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) Electrospun Membranes: Fabrication and Characterization. *Materials Science and Engineering C*. 61: 396-410.

[20] Lim, M. M. & Sultana, N. 2016. In Vitro Cytotoxicity And Antibacterial Activity Of Silver-Coated Electrospun Polycaprolactone/gelatine Nanofibrous Scaffolds. *3 Biotech*. 6: 211. doi:10.1007/s13205-016-0531-6.